PROPERTIES OF MIXTURES OF NORMAL BUTYL ALCOHOL AND WATER; RECOVERY OF NORMAL BUTYL ALCOHOL FROM WATER MIXTURES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED Properties of Mixtures or Normal Butyl Alcohol and Water; Recovery of Normal Butyl Alcohol from Water Mixtures.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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I. Introduction.

Normal butyl alcohol is becoming more and more important in organic chemistry, especially as a solvent for various substances and the recovery of this solvent promises to develop into an important consideration in commercial use. It was with this idea in mind that the following work was done concerning the physical properties and recovery of the normal butyl alcohol.

Until quite recently, very little was to be found in the literature concerning this alcohol and the writer feels that the work is among the first that have been done on this subject. Hereafter in this article the word alcohol will be used to denote normal butyl alcohol only.

Normal butyl alcohol is manufactured by a fermentation process in which acetone and alcohol , particularly butyl alcohol, are obtained by fermentation under aerobic or anaerobic conditions of carbohydrate material such as maize, rice, wheat, oats, potatoes, etc., with a culture of the bacteria which are found in soil or on cereals such as maize, rice and flax. The bacteria will also liquefy gelatin and are stated to be probably Bacillus granulobacter pectinovorum.

The production of this alcohol is now carried on at a comparatively low cost. The price in 1917 was $2.10 for 10 grams and now the cost is only $5.00 per gallon.

II. Dehydration of Normal Butyl Alcohol.

In making anhydrous alcohol, the following proceedure was used. The usual method of treatment with lime was first used. The alcohol refluxed with fresh lime for several hours and then distilled through an efficient rectifying column. This was then refluxed over metallic calcium and the distillation through the rectifying column repeated until a constant boiling point was obtained. It is believed that alcohol so prepared contains only a small fraction of one per cent of water. This small quantity of waterwould not make an appreciable error in the specific gravity determinations of the alcohol-water mixtures.

The partial dehydration by means of lime gives an alcohol of about 99.5 % and for all practical purposes this is probably pure enough. However, in order to obtain a purer product, the alcohol is refluxed over metallic calcium and redistilled. This removes all the water.

No satisfactory test was found for the detection of slight amounts of water in the alcohol. The copper sulfate test was found to be indecisive while the benzene test could not detect water unless the water was present in an amount greater than 5 %.

III. Density of Alcohol-Water Mixtures.

The alcohol-water mixtures were made by weighing the water and alcohol in stoppered bottles. The stoppers were then made secure and the solutions thoroughly mixed for several hours by means of a mechanical shaker which insured complete solution of the respective liquids in each other.

Then the specific gravity was determined of the solutions in each bottle in which only one layer was present. A Westphal balance was used for the specific gravity determinations. The alcohol will dissolve 19.8 % of water and water will dissolve 7.25 % alcohol.

The results of these determinations are shown below.

Water Layer.

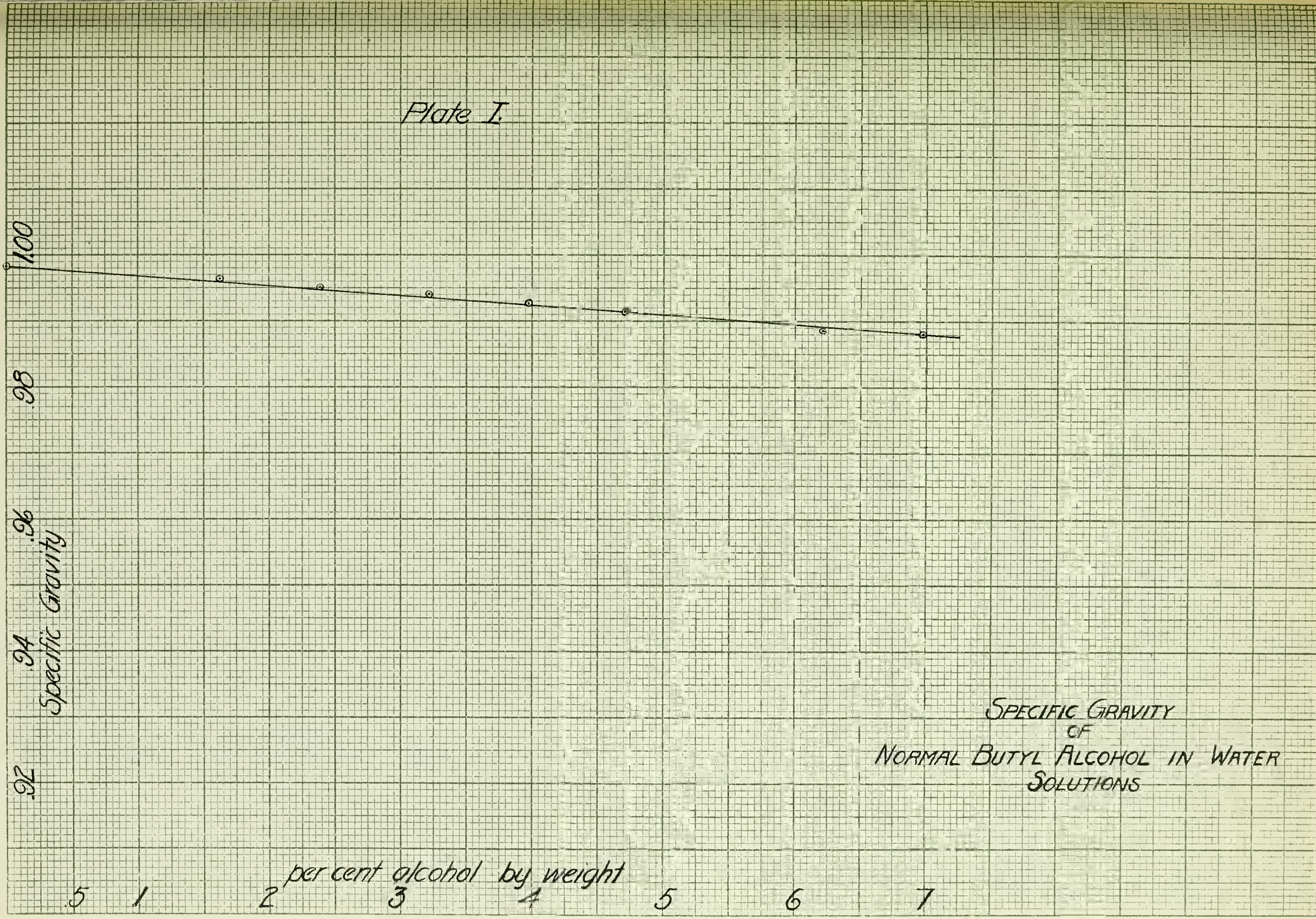
Wt. % alcohol	sp. gr.	Wt. % alcohol	sp, gr.
1.63	0.9963	4.71	0.9911
2.39	0.9950	6.22	0.9888
3.21	0.9930	6.98	0.9880
3.97	0.9927		

Alcohol Layer.

Wt.% alcohol	sp. gr.	Wt.% alc.	sp. gr.
98.1	0.8100	87.8	0.8298
96.6	0.8130	86.5	0.8322
93.4	0.8191	85.7	0.8345
92.2	0.8210	82.8	0.8390
90.8	0.8248	80.2	0.8445
89.3	0.8275		

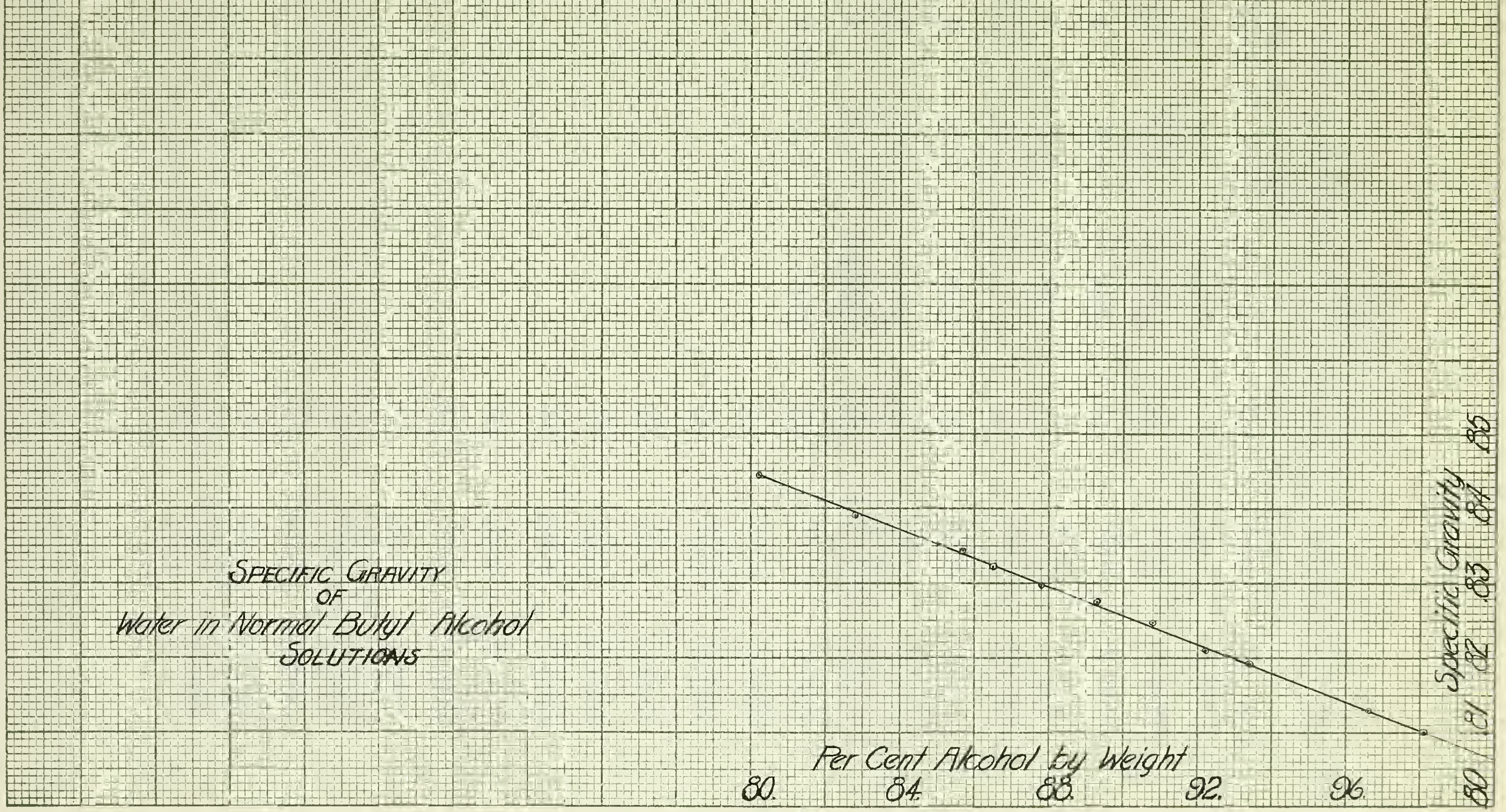
These results were plotted on cross-section paper (Plates I and II) so that 0.1 % could be easily read on the abscissa and 0.0002 sp.gr. on the ordinate. A straight line curve was drawn to connect the points and from these Table I was constructed, giving the specific gravity for each percentage by weight of alcohol and the corresponding volume percentage.

Plate I.



1.00
.98
.96
.94
.92
Specific Gravity
.5
1
2
3
4
5
6
7
per cent alcohol by weight
SPECIFIC GRAVITY
OF
NORMAL BUTYL ALCOHOL IN WATER
SOLUTIONS

Plate II.



Specific Gravity
of
Water in Normal Butyl Alcohol
Solutions
Per Cent Alcohol by Weight
80.
84.
88.
92.
96.
Specific Gravity
.80
.81
.82
.83
.84
.85

Table I.

Specific Gravity of Normal Butyl Alcohol-Water Mixtures.

Wt. % alcohol	Vol. % alc.	sp. gr.	Wt. % alc.	Vol. % alc.	sp. gr.
0	0.0	0.9984	100	100	0.8063
1	1.2	0.9969	99	99.3	0.8082
2	2.5	0.9953	98	98.5	0.8103
3	3.7	0.9939	97	97.6	0.8121
4	4.9	0.9923	96	96.8	0.8140
5	6.1	0.9910	95	95.9	0.8160
6	7.3	0.9895	94	95.1	0.8179
7	8.6	0.9880	93	94.3	0.8199
7.25	8.8	0.9878	92	93.4	0.8218
			91	92.6	0.8238
			90	91.8	0.8256
			89	91.0	0.8275
			88	90.1	0.8295
			87	89.3	0.8314
			86	88.4	0.8333
			85	87.5	0.8352
			84	86.7	0.8372
			83	85.8	0.8391
			82	85.0	0.8410
			81	84.1	0.8430
			80.2	83.2	0.8445

IV. Boiling Points of Alcohol-Water Mixtures.

The same solutions that were used for the determination of the specific gravities were also used for the determination of the boiling points of solutions of varying concentration. The solution was placed in a flask which was fitted with a condenser in order to keep the concentration of the liquid constant. The boiling point was taken and corrections made for pressure differences from 760 mm, for stem exposure, and for calibration of the thermometer used.

The thermometer was calibrated with water and a constant correction of $+ 0.4^{\circ}$ found. The observed temperatures were corrected for exposed mercury column by adding $N(t-t').000154$, where N is the length of the exposed mercury in degrees, t the observed temperature, and t' the room temperature. A correction for pressure was calculated from $dT = CT_{B_0} (760 - P)$ where dT is the correction, C a constant, T_{B_0} the boiling point of the liquid, and P the observed pressure.

Table II shows the data in tabular form and the experimental values were used to construct the boiling point curve which is shown on the graph paper (Plate III).

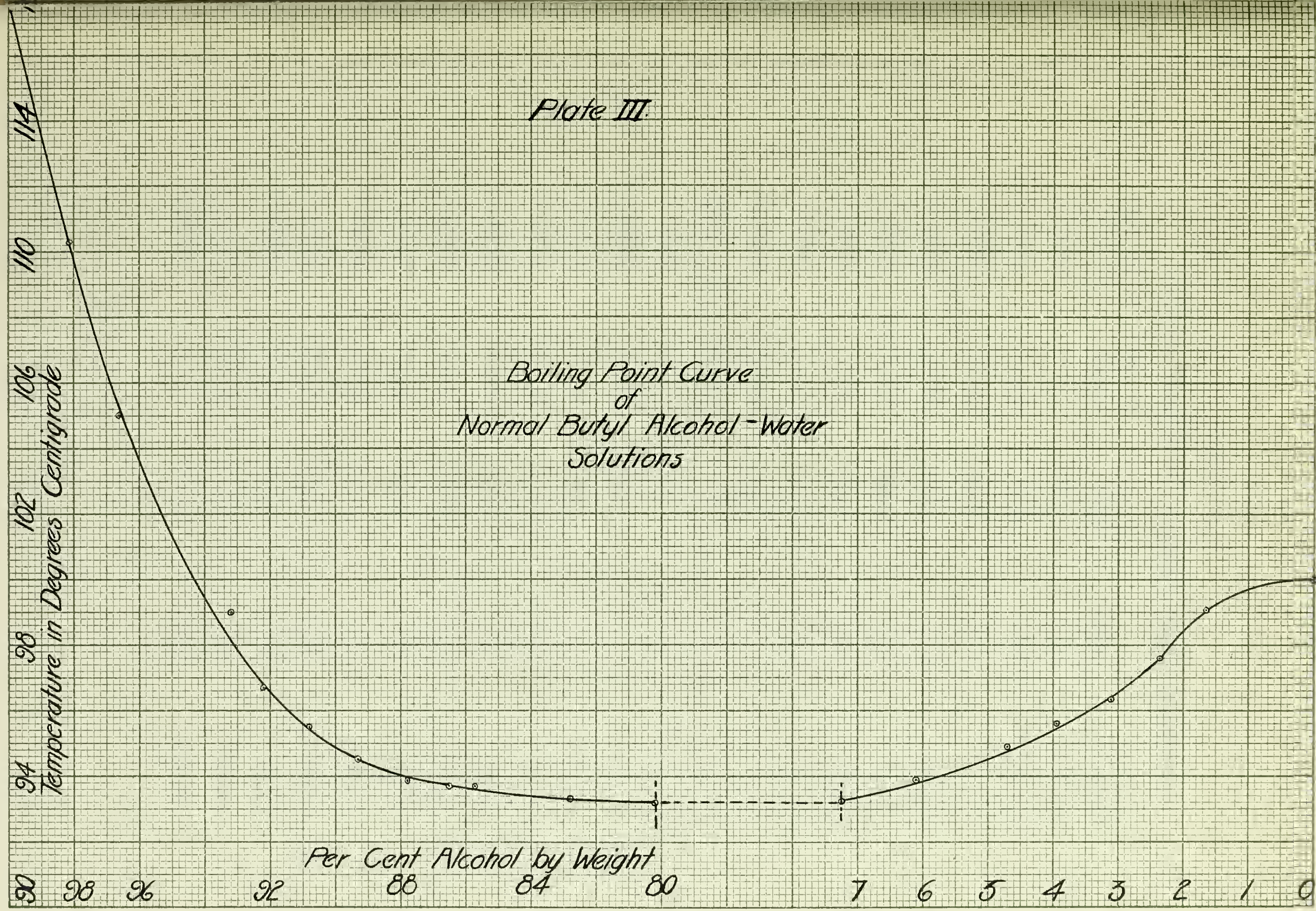


Plate III
Boiling Point Curve
of
Normal Butyl Alcohol-Water
Solutions
Temperature in Degrees Centigrade
114
110
106
102
98
94
Per Cent Alcohol by Weight
98
96
92
88
84
80
7
6
5
4
3
2
1
0

Table II.

Boiling Points of Alcohol-Water Mixtures.

Sp. Gr. (curve)	Wt. % alc.	B. P. (obs)	Corr.	B. P. (corr)
0.9984	0.0	98.7	1.30	100.00
0.9960	1.63	97.8	1.27	99.07
0.9947	2.39	96.3	1.24	97.54
0.9935	3.21	95.1	1.28	96.38
0.9924	3.97	94.4	1.20	95.60
0.9915	4.71	93.7	1.18	94.88
0.9891	6.22	92.8	1.16	93.96
0.9880	6.98	92.2	1.16	93.36
Mixt. both layers		92.1	1.16	93.26
0.8100	98.1	108.0	2.24	110.24
0.8130	96.6	103.0	2.00	105.0
0.8191	93.4	97.0	2.00	99.0
0.8214	92.2	94.8	1.93	96.73
0.8240	90.8	93.6	1.90	95.50
0.8270	89.3	92.6	1.87	94.47
0.8298	87.8	92.0	1.87	93.87
0.8325	86.5	91.8	1.86	93.66
0.8340	85.7	91.8	1.86	93.66
0.8395	82.8	91.4	1.85	93.25
0.8445	80.2	91.3	1.94	93.24
0.9984	0.0	98.0	2.00	100.00

VI. Fractional Distillation.

The alcohol is recovered from the water mixtures by means of fractionation through an efficient rectifying column. In a trial run, large amounts of alcohol and water were thoroughly mixed and 750 cc of the top layer were taken for the determination. This layer contained 80.2 per cent alcohol. The first portions of the distillate contained 40 per cent of water as conpared to 20 per cent in the original liquid in the flask. This proportion remained constant until all the water distilled over and then the pure alcohol was collected.

The top layers of each portion were mixed and the fractionation repeated, giveng more of the pure liquid. Then the water layers from each portion were added together and distilled and all the alcohol came over quickly in an 80.2 per cent mixture. This was added to the other portions rich in alcohol and the distillation carried out a third time.

The time required for the distillations is not excessive and four distillations yield about 90 per cent of the alcohol in the original mixture in a pure form.

VI. Summary.

1. The specific gravity of normal butyl alcohol was found to be 0.8064 at 25° C. Tobin gives 0.8057 and Wad and Gokhale 0.8066.
2. The boiling point was found to be 117.4° at 760 mm pressure. Doroshevski and Dvorzhanchik give 117.1°, Kahlbaum gives 117.6°, and Tobin gives 117.71°,
3. Tables for specific gravities and for boiling points of alcohol-water mixtures are given.
4. The alcohol is only partially miscible with water. Two layers are formed which contain 80.2 per cent and 7.25 per cent of alcohol.
5. Curves for specific gravities and for boiling points of the varying concentrations are given.
6. The alcohol may be recovered from water mixtures by fractionation.

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